Description

Thermally insulating material and arrangement of a thermal barrier coating incorporating said thermally insulating material

The invention relates to a thermally insulating material for a thermal barrier coating of a substrate for limiting heat transfer between the substrate and an environment of the substrate, the thermally insulating material having at least one luminophore which can be excited to emit luminescent light at a particular emission wavelength, and the luminophore having at least one metal oxide with at least one trivalent metal A. In addition to the thermally insulating material, an arrangement of at least one thermal barrier coating incorporating the thermally insulating material on a substrate is specified.

A thermally insulating material and an arrangement of this kind are known from EP 1 105 550 B1. The substrate is a component in a gas turbine. The substrate is made of metal. High temperatures in excess of 1200° C occurring in a gas turbine in the environment of the component may cause the metal of the component to be damaged. In order to prevent this, a thermal barrier coating (TBC) is deposited on the component. The thermal barrier coating ensures that a reduced heat exchange takes place between the metal substrate and the environment, causing a metal surface of the component to heat less strongly. On the metal surface of the component, a surface temperature occurs which is lower than the temperature in the environment of the component.

The thermally insulating material constitutes a base material of the thermal barrier coating. The mechanical and thermal

properties of the thermal barrier coating depend essentially on the properties of the thermally insulating material. The base material of the known thermal barrier coating is a metal oxide. The metal oxide is, for example, an yttrium stabilized zirconium oxide (YSZ). This thermally insulating material has a thermal conductivity of between 1 and 3 W/m·K. In order to ensure efficient protection of the substrate, the layer thickness of the thermal barrier coating is approximately 250 µm. As an alternative to yttrium stabilized zirconium oxide, a metal oxide in the form of an yttrium aluminum granate is specified as the thermally insulating material.

In order to bond the thermal barrier coating and the substrate firmly together, a metal alloy interlayer (bond coat) is deposited on the surface of the component. To improve the bond, a ceramic interlayer of a ceramic material such as aluminum oxide can be additionally disposed between the thermal barrier coating and the component.

A so-called thermoluminescent indicator is embedded in the thermal barrier coating. This indicator is a luminescent material (luminophore) which can be stimulated to emit a luminescent light with a particular emission wavelength by excitation with excitation light of a particular excitation wavelength. The excitation light is, for example, UV light. The emission light is, for example, visible light. The luminophore used is a so-called recombination luminescence material. The luminescent process is initiated by electronic transitions between energy states of the activator. A luminophore of this kind consists, for example, of a solid with a crystal lattice (host lattice) in which a so-called activator is embedded. The solid body is doped with the activator. The activator participates together with the entire solid body in the luminescent process of the luminophore.

With the known thermal barrier coating, the base material of the thermal barrier coating is doped with an activator. A thermal barrier coating consisting of the luminophore is present. The activator used is a rare earth element. In the case of yttrium stabilized zirconium oxide, the rare earth element is typically europium. The thermally insulating material yttrium aluminum granate is doped with the rare earth elements dysprosium or terbium.

The known thermal barrier coating utilizes the fact that an emission property of the luminescent light of the luminophore, e.g. an emission intensity or emission decay time, is dependent on the temperature of the luminophore. On the basis of this dependence, the luminophore can be used to indicate the temperature of the thermal barrier coating. To ensure that this relationship can be established, the thermal barrier coating is optically accessible to excitation light in the UV range. It is simultaneously ensured that the luminescent light of the luminophore can be radiated and detected by the thermal barrier coating.

For example, in order to ensure optical accessibility, a single thermal barrier coating containing the luminophore is disposed on the substrate. As an alternative solution, an additional thermal barrier coating which is transparent to the excitation light and the luminescent light of the luminophore is deposited on the thermal barrier coating. The luminescent light of the luminophore can penetrate the additional thermal barrier coating.

Because of specific material properties such as phase stability or sintering tendency, usability of a thermal barrier coating consisting of one of the abovementioned

thermally insulating luminescent materials is limited to an operating temperature of approximately 1200° C. These thermally insulating materials are therefore unsuitable for future gas turbine generations where the operating temperature will have to be increased to improve efficiency.

The object of the present invention is therefore to specify a thermally insulating luminescent material, which is stable above a temperature of 1200° C, for a thermal barrier coating of a substrate.

This object is achieved by a thermally insulating material for a thermal barrier coating of a substrate for reducing heat transfer between the substrate and an environment of the substrate, the thermally insulating material having at least one luminophore which can be excited to emit luminescent light at a particular emission wavelength, and the luminophore having at least one metal oxide with at least one trivalent metal A. The thermally insulating material is characterized in that the metal oxide is a mixed oxide selected from the perovskite group with the empirical formula $AA'O_3$ and/or pyrochlore with the empirical formula $A_2B_2O_7$, A' being a trivalent metal and B a tetravalent metal.

This object is also achieved by an arrangement of at least one thermal barrier coating on a substrate for reducing heat transfer between the substrate and an environment of the substrate, the thermal barrier coating containing the described thermally insulating material incorporating the luminophore.

A thermal barrier coating consisting of a perovskite and/or a pyrochlore (pyrochlore phase) is characterized by high stability at temperatures in excess of 1200° C. These stable

thermal barrier coatings have a luminophore. The thermal barrier coating can be a single or multiphase system. Single phase means that a TBC ceramic phase constituted by the thermally insulating material essentially consists of the luminophore only. The thermally insulating material of the thermal barrier coating is the luminophore. In the case of a multiphase thermal barrier coating, the thermally insulating material and the luminophore are different. The thermally insulating material contains luminophoric particles from the luminophore. The ceramic phase is constituted by different materials. The luminophoric particles are preferably distributed homogeneously over the thermal barrier coating. It is advantageous, moreover, if the thermally insulating material and the luminophore consist of an essentially identical kind of solid. The luminophore and the thermally insulating material consist of the same metal oxide. The two materials differ solely in respect of their optical characteristics. The luminophore is doped, for example, for this purpose.

The luminophore is a recombination luminescence material, the emission of the luminescent light being preferably based on the presence of an activator. Using an activator or a plurality of activators, the emission properties of the luminophore, such as the emission wavelength and the emission intensity, can be varied relatively easily. In a particular embodiment, to excite the emission of luminescent light the luminophore has an activator selected from the cerium and/or europium and/or dysprosium and/or terbium group. Because of their ion radii, rare earth elements can generally be easily incorporated in the crystal lattice of perovskites and pyrochlores. Activators in the form of rare earth elements are therefore generally suitable. The rare earth elements

specified have shown themselves to be particularly good activators.

When using an activator, its proportion in the luminophore must be selected such that the thermal and mechanical properties of the metal oxide of the luminophore are virtually unaffected. The mechanical and thermal properties of the metal oxide are retained in spite of doping. In a particular embodiment, the proportion of activator in the luminophore is up to 10 mol%.

The proportion is preferably less than 2 mol%, e.g. 1 mol%. This low proportion of activator has been found sufficient to achieve a usable emission intensity of the luminophore while retaining the thermal and mechanical stability of a thermal barrier layer produced using the luminophore.

In a particular embodiment, the trivalent metal A and/or the trivalent metal A' is a rare earth element Re. The trivalent metal A and/or the trivalent metal A' is specifically a rare earth element selected from the lanthanum and/or gadolinium and/or samarium group. Other rare earth elements are likewise conceivable. By using a perovskite and/or a pyrochlore with rare earth elements, an activator in the form of a rare earth element can be easily incorporated in the crystal lattice of the perovskite or pyrochlore because of the similar ion radii.

One of the trivalent metals A and A' of the perovskite is a main group or subgroup element. The tetravalent metal B of the pyrochlore is likewise a main or subgroup element. In both cases, mixtures of different main and subgroup elements can be provided. Because of the different ion radii, the rare earth elements and the main or subgroup elements preferably assume different positions in the perovskite or pyrochlore crystal

lattice, aluminum having been found to be particularly advantageous as a trivalent main group element. Together with rare earth elements, aluminum forms, for example, a perovskite which produces a mechanically and thermally stable thermal barrier coating. In a particular embodiment, the perovskite is therefore a rare earth aluminate. The empirical formula is $ReAlO_3$, with Re standing for a rare earth element. The rare earth aluminate is preferably a gadolinium lanthanum aluminate. The empirical formula is typically $Gd_{0.25}La_{0.75}AlO_3$. Specifically the subgroup elements hafnium and/or titanium and/or zirconium are used as the tetravalent metal B of the pyrochlore. The pyrochlore is therefore advantageously selected from the rare earth titanate and/or rare earth hafnate and/or rare earth zirconate group. The rare earth zirconate is specifically selected from the gadolinium zirconate and/or samarium zirconate group. The preferred empirical formulae are $Gd_2Zr_2O_7$ and $Sm_2Zr_2O_7$. The rare earth hafnate is preferably lanthanum hafnate. The empirical formula is $La_2Hf_2O_7$.

The luminophore is optically excited to emit luminescent light, said luminophore being irradiated with excitation light of a particular excitation wavelength. By absorbing the excitation light, the luminophore is excited to emit luminescent light. The excitation light is e.g. UV light and the luminescent light low-energy visible light.

The excitation of the luminophore with excitation light lends itself to checking the condition of a luminophore-containing thermal barrier coating optically accessible to the excitation light and the luminescent light. For this purpose, e.g. only the thermal barrier coating containing the luminophore is deposited on the substrate.

In a particular embodiment in respect of the arrangement of thermal barrier coating on the substrate, at least one other thermal barrier coating is present which is essentially luminophore-free, essentially free meaning that, due to a very low proportion of luminophore, no analyzable luminescent light can be detected. The additional thermal barrier coating can be disposed between the substrate and the thermal barrier coating containing the luminophore. The outer thermal barrier coating is formed by the thermal barrier coating containing the luminophore. Any transmission property of the additional thermal barrier coating in respect of the luminescent light and/or the excitation light is irrelevant. The thermal barrier coating containing the luminophore is optically accessible. A solution of this kind is advantageous, for example, for a thermal barrier coating comprising a pyrochlore. In order to achieve a firm bond between the thermal barrier coating and a metallic interlayer deposited on the substrate, an additional thermal barrier coating consisting of an yttrium stabilized zirconium oxide is deposited directly on the metallic interlayer. The thermal barrier coating containing the luminophore is deposited over this additional thermal barrier coating.

However, the additional thermal barrier coating can also be transparent to the excitation light and the luminescent light of the luminophore. The excitation light and the luminescent light can penetrate through the additional thermal barrier coating. For a solution of this kind, the thermal barrier coating can be disposed between the additional thermal barrier coating and the substrate. Due to the transmission property of the additional thermal barrier coating, the thermal barrier coating containing the luminophore is continuously optically accessible. In this way, as in the cases in which only the

thermal barrier coating containing the luminophore is present or the thermal barrier coating containing the luminophore forms the outer thermal barrier coating of a multilayer structure, the condition of the thermal barrier coating can be determined by observing one of the emission properties of the luminescent light. Thus, for example, the temperature of the thermal barrier coating can be indicated.

In a particular embodiment, the additional thermal barrier coating is opaque to the excitation light for stimulating the luminophore to emit luminescent light and/or to the luminescent light of the luminophore. Because of the transmission or absorption properties of the additional thermal barrier coating, the excitation light and/or the luminescent light cannot penetrate, or only a small portion of it can penetrate, the additional thermal barrier coating. In a particular embodiment, the thermal barrier coating is disposed between the substrate and the additional thermal barrier coating in such a way that the excitation light of the luminophore and/or the luminescent light of the luminophore can essentially only reach the environment of the substrate through orifices in the additional thermal barrier coating. Such orifices are, for example, cracks or gaps in the additional thermal barrier coating. Also conceivable is an orifice caused by erosion of other thermally insulating material of the additional thermal barrier coating. These orifices can easily be made visible by illuminating the arrangement with the excitation light. At the locations in which the UV light reaches the thermal barrier coating through the orifices, the luminophore is excited to emit luminescent light. The luminescent light passes again through the orifices to the environment of the substrate where it can be detected. Because of the orifices, luminescent light occurs which stands out clearly from the background.

During an idle time of an equipment, the thermal barrier coating of a substrate used in the equipment can be checked in a simple and reliable manner in the way described. The equipment can be e.g. a gas turbine, the substrate e.g. a gas turbine blade. The multilayer system comprised of the thermal barrier coatings is disposed on the turbine blade. By illuminating the turbine blade and observing the luminescent light of the luminophore, the locations in the additional, outermost thermal barrier coating which have orifices become visible.

It is also conceivable for the condition of the thermal barrier coating to be checked during operation of the equipment. For this purpose, for example, a combustion chamber of the above-described gas turbine in which the turbine blades are installed is provided with a window through which the luminescence of the luminophore can be observed. The occurrence of luminescent light indicates that the additional, outermost thermal barrier coating of at least one turbine blade has a crack or gap or is eroded.

A further advantage of the described arrangement is that, as a result of advanced erosion, the thermally insulating material containing the luminophore is also eroded away. By means of suitable detectors, the luminophore can be detected in an exhaust gas of the gas turbine. This is an indication that erosion has advanced as far as the thermal barrier coating containing the luminophore.

In a particular embodiment, the substrate is a component of an internal combustion engine, such as a diesel engine. In a particular embodiment, the internal combustion engine is a gas turbine, the substrate being e.g. a tile with which a

combustion chamber of the gas turbine is clad. The substrate is in particular a blade of the gas turbine, it being conceivable that the different substrates are provided with thermal barrier coatings containing luminophores which emit different luminescent light, thereby enabling the component on which damage is present to be easily determined.

To deposit the various layers, in particular the thermal barrier coating and the additional thermal barrier coating, any coating process can be used. The coating process is in particular plasma spray coating. It can also be a vapor deposition process, such as PVD (physical vapor deposition) or CVD (chemical vapor deposition). Using the method described, thermal barrier coatings with layer thicknesses of 50 to 600 µm or more can be deposited.

To summarize, the particular advantages of the invention are as follows:

- The materials used are stable at temperatures of over 1200° C, making them particularly suitable for use in internal combustion engines, e.g. in a gas turbine.

- The metal oxides used are selectively doped with activators, thereby yielding thermal barrier coatings containing luminescent substances that are thermally and mechanically stable even at temperatures above 1200° C and which can be used to check the condition of the thermal barrier coatings during operation but also when the substrate is not in operation.

The invention will now be explained in greater detail with reference to several examples and the accompanying drawings which are schematic and not to scale.

Figures 1 to 3 each show a detail of a lateral cross-section of an arrangement of a thermal barrier coating comprising a thermally insulating material containing a luminophore.

The arrangement 1 consists of a substrate 2 on which a thermal barrier coating 3 is disposed (Figure 1). The substrate 2 is a turbine blade of a gas turbine. The turbine blade is made of metal. In the combustion chamber of the gas turbine, which constitutes the environment 7 of the substrate 2, temperatures of over 1200° C can occur during operation of the gas turbine. The thermal barrier coating 3 is present in order to prevent the surface 8 of the substrate 2 from overheating. The thermal barrier coating 3 is used to limit heat transfer between the substrate 2 and the environment 7 of the substrate 2.

A metal alloy interlayer 4 (bond coat) is deposited between the thermal barrier coating 3 and the substrate 2. The thermal barrier coating 3, the interlayer 4 and possibly the additional thermal barrier coating 5 are deposited on the surface 8 of the substrate 2 using a plasma spray process.

Example 1:

The thermally insulating material of the thermal barrier coating 3 is a metal oxide in the form of a rare earth aluminate with the empirical formula $Gd_{0.25}La_{0.75}AlO_3$. According to a first embodiment, the rare earth aluminate is mixed with 1 mol% Eu_2O_3. The rare earth aluminate has the activator europium in a proportion of 1 mol%. Exciting the luminophore with UV light results in a red luminescent light with an emission maximum at around 610 nm. The excitation wavelength is typically 254 nm.

According to an alternative embodiment, the rare earth aluminate is doped with 1 mol% terbium, resulting in a luminophore with green luminescent light having an emission wavelength at 544 nm.

Example 2:

In contrast to the previous example, a multilayer structure of the thermal barrier coating 3 and an additional thermal barrier coating 5 is present on the substrate 2 (Figure 2). The thermal barrier coating 3 consists of a pyrochlore. The pyrochlore is a gadolinium zirconate with the empirical formula $Gd_2Zr_2O_7$. To produce the luminophore, the pyrochlore is mixed with 1 mol% Eu_2O_3. The gadolinium zirconate has the activator europium in a proportion of 1 mol%.

To improve the adhesion of the substrate 2, an additional thermal barrier coating 5 is present between the bond coat 4 and the thermal barrier coating 3 containing the luminophore. The additional thermal barrier coating 5 consists of yttrium stabilized zirconium oxide.

Example 3:

A multilayer structure is likewise present (Figure 3). Unlike in the previous example, the thermal barrier coating 3 containing the luminophore is disposed between the additional thermal barrier coating 5 and the substrate 2. The additional thermal barrier coating 5 is opaque to the excitation light and/or the luminescent light of the luminophore. The luminescent light of the luminophore can only be detected in the environment of the substrate if the additional thermal barrier coating 5 has an orifice 6.